Modeling and Parameter Estimation of Batch Solid-Liquid Reactors

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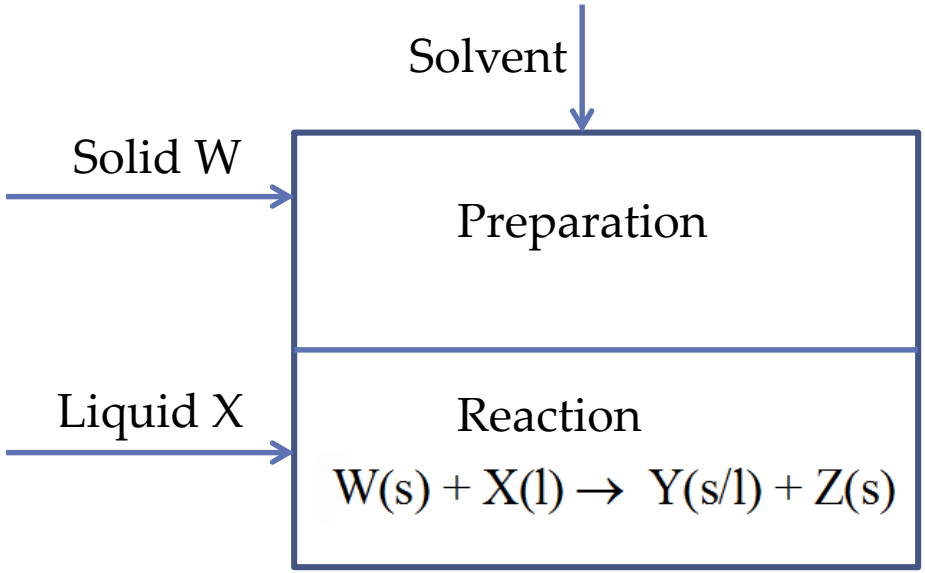
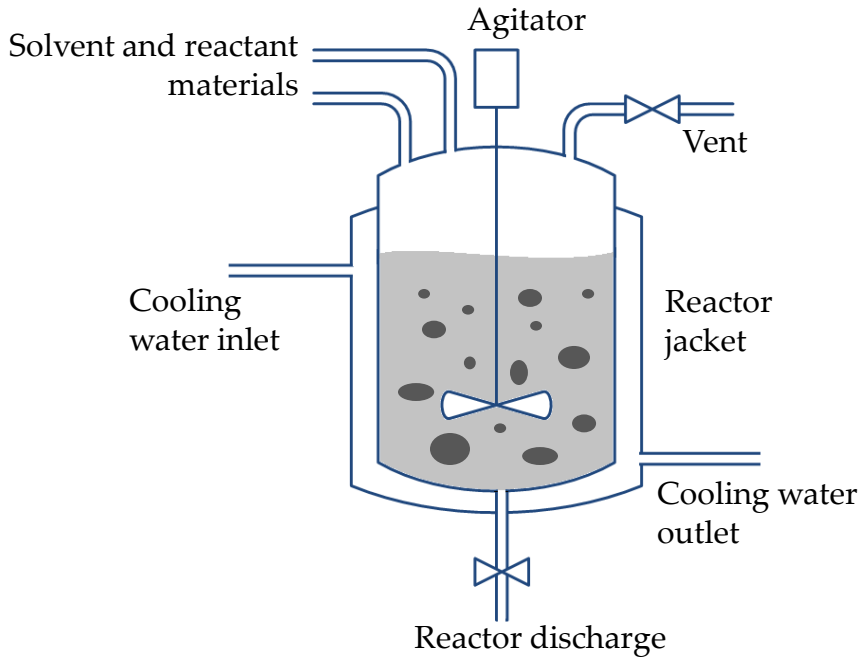
Problem Statement

- Batch reactor





Solid-liquid Reactions

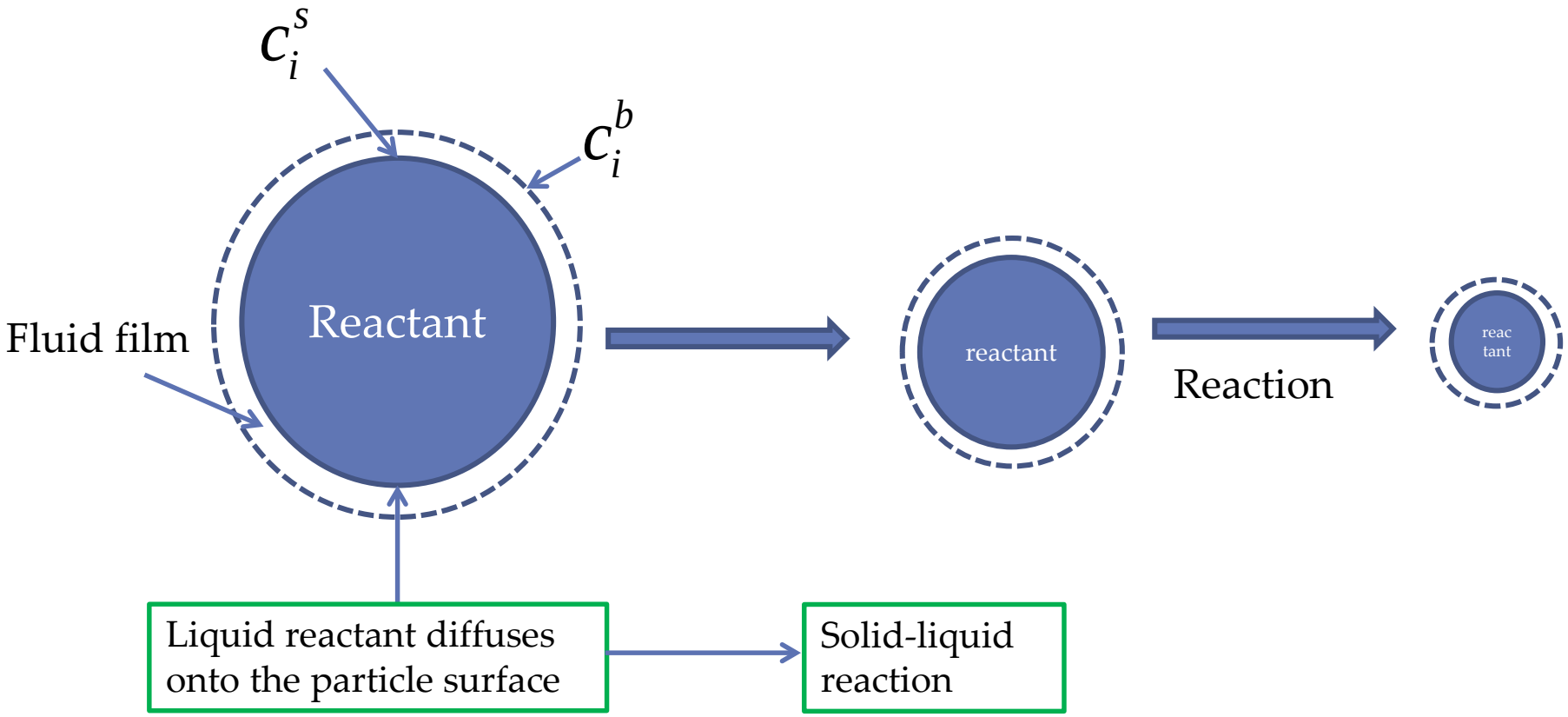
Solid and liquid reactants react to generate solid or liquid products

$$W(s) + X(l) \rightarrow Y(s/l) + Z(s)$$

- **Surface reaction, dissolution, diffusion** -- where does the reaction occur, on the solid surface or in the liquid phase?
- **Different particle shapes and sizes** -- how to incorporate reaction surface?
- **Product effects** – where are the products, accumulating on the reaction surface or cracking off?

Reaction Mechanism 1

Shrinking particle model



Reaction Mechanism 1

Shrinking particle model

- Pseudo-steady state is assumed on the reaction surface.

$$k_{dl}(c_l^b - c_l^s) + \sum_{k=1}^{K} \upsilon_{lk} R_k = 0$$ Fick's Law

Reaction rate R_k is a function of surface concentration of the liquid reactant

- Total surface area is related to total amount and the shape of particles.

$$S = \sigma M_s N_{s0}^{1/a} N_s^{1-1/a}$$

σ is the specific surface area with the unit [m^2/kg].
a is a dimensionless shape factor.

Reaction Mechanism 1

Shrinking particle model

Solid: $$\frac{dN_s}{dt} = \sum_{k=1}^{K} \upsilon_{sk} SR_k = \sum_{k=1}^{K} \upsilon_{sk} \sigma_s M_s N_{s0}^{1/a_s} N_s^{1-1/a_s} k_{0k} e^{-\frac{E_{ak}}{RT}} (c_l^s)^{\alpha_k}$$

Liquid: $$\frac{dN_l}{dt} = \sum_{k=1}^{K} \upsilon_{lk} SR_k = \sum_{k=1}^{K} \upsilon_{lk} \underbrace{\sigma_s M_s N_{s0}^{1/a_s} N_s^{1-1/a_s}}_{\text{Surface area}} \underbrace{k_{0k} e^{-\frac{E_{ak}}{RT}} (c_l^s)^{\alpha_k}}_{\text{Reaction rate}}$$

$$k_{dl}(c_l^b - c_l^s) + \sum_{k=1}^{K} \upsilon_{lk} R_k = 0$$

$$c_l^b = \frac{N_l}{V_l}$$

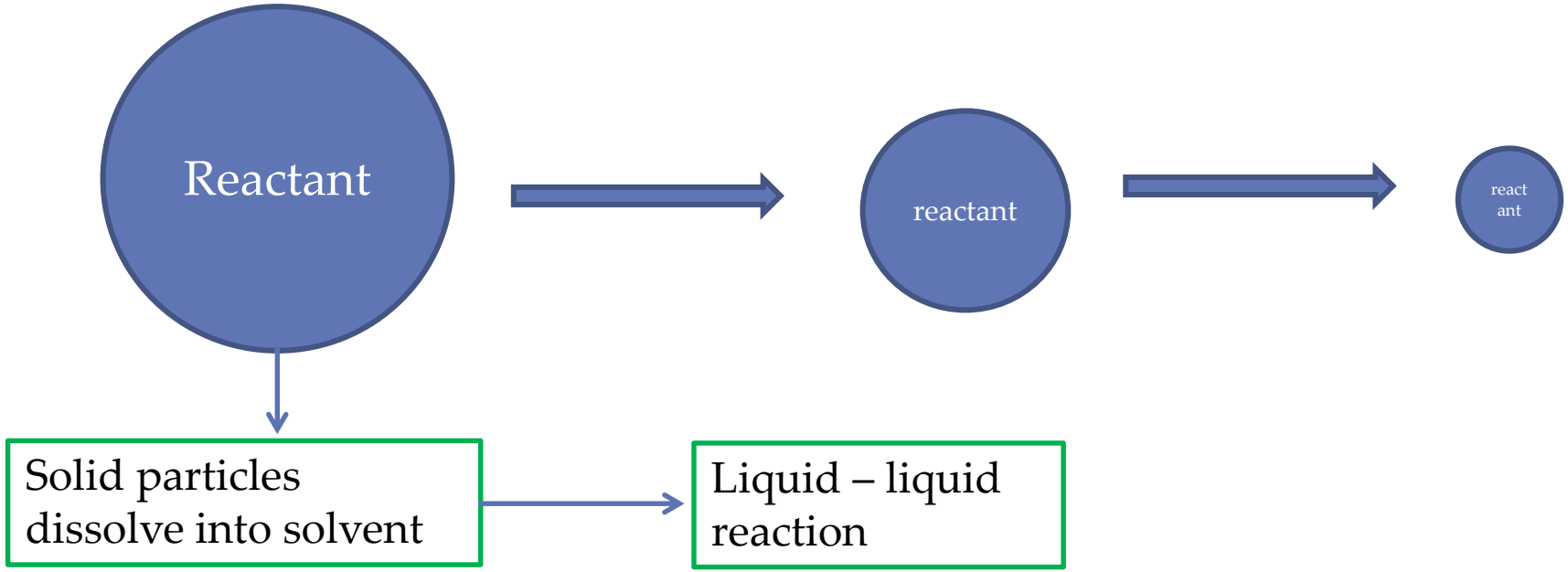
Surface reaction rate depends on surface concentration of the liquid reactant.

$$R_k = k_k (c_l^s)^{\alpha_k}$$

$$k_k = k_{0k} e^{-\frac{E_{ak}}{RT}}$$

Reaction Mechanism 2

Dissolution model



Reaction Mechanism 2

Dissolution model

- Assume dissolution is the rate limiting step. (Reaction is much faster than dissolution.)

$$\frac{dN_s}{dt} = -kS \qquad S = \sigma M_s N_{s0}^{1/a} N_s^{1-1/a}$$

- Dissolution rate constant is Arrhenius type. $k = k_0 e^{-\frac{E_a}{RT}}$

Solid: $$\frac{dN_s}{dt} = \sum_{k=1}^{K} \upsilon_{sk} \sigma_s M_s N_{s0}^{1/a_s} N_s^{1-1/a_s} k_0 e^{-\frac{E_a}{RT}}$$

Liquid: $$\frac{dN_l}{dt} = \sum_{k=1}^{K} \upsilon_{lk} \underbrace{\sigma_s M_s N_{s0}^{1/a_s} N_s^{1-1/a_s}}_{\text{Surface area}} \underbrace{k_0 e^{-\frac{E_a}{RT}}}_{\text{Dissolution rate}}$$

Dissolution rate doesn't depend on surface concentration of the liquid reactant.

Batch Reactor Model

Lumped parameters A, B, D, E, F and heat transfer coefficient U are to be estimated.

$$U = \phi(T, \mathbf{U_A}, \mathbf{U_B}, \mathbf{U_C})$$

Solid reactant $$\frac{dN_W}{dt} = -\mathbf{A}N_W^{\mathbf{E}} exp(\mathbf{B}(1-\frac{Tr}{T}))C_{s,X}^{\mathbf{F}}$$

Liquid reactant $$\frac{dN_X}{dt} = F_{in,X} - \mathbf{A}N_W^{\mathbf{E}} exp(\mathbf{B}(1-\frac{Tr}{T}))C_{s,X}^{\mathbf{F}}$$

Product $$\frac{dN_Y}{dt} = \mathbf{A}N_W^{\mathbf{E}} exp(\mathbf{B}(1-\frac{Tr}{T}))C_{s,X}^{\mathbf{F}}$$

Volume $$\frac{dV}{dt} = Q_{in}$$

Temperature $$\frac{dT}{dt} = \frac{\sum \Delta H_j r_j V + \sum F_k M w_k C p_k (T_{in} - T) + \mathbf{U} a_{jac} (\bar{T}_{jac} - T)}{\sum N_i M w_i C p_i}$$

Diffusion $$\mathbf{D}(C_{b,X} - C_{s,X}) - exp(\mathbf{B}(1-\frac{Tr}{T}))C_{s,X}^{\mathbf{F}} = 0$$

Batch Reactor Model

One formulation for two mechanisms

F=0 → Dissolution model
F>0 → Shrinking particle model

Solid reactant $\frac{dN_W}{dt} = -\mathbf{A}N_W^{\mathbf{E}} exp(\mathbf{B}(1-\frac{Tr}{T}))C_{s,X}^{\mathbf{F}}$

Liquid reactant $\frac{dN_X}{dt} = F_{in,X} - \mathbf{A}N_W^{\mathbf{E}} exp(\mathbf{B}(1-\frac{Tr}{T}))C_{s,X}^{\mathbf{F}}$

Product $\frac{dN_Y}{dt} = \mathbf{A}N_W^{\mathbf{E}} exp(\mathbf{B}(1-\frac{Tr}{T}))C_{s,X}^{\mathbf{F}}$ → Surface concentration of liquid reactant

Volume $\frac{dV}{dt} = Q_{in}$

Temperature $\frac{dT}{dt} = \frac{\sum \Delta H_j r_j V + \sum F_k Mw_k Cp_k (T_{in}-T) + \mathbf{U}a_{jac}(\bar{T}_{jac}-T)}{\sum N_i Mw_i Cp_i}$

Diffusion $\mathbf{D}(C_{b,X}-C_{s,X}) - exp(\mathbf{B}(1-\frac{Tr}{T}))C_{s,X}^{\mathbf{F}} = 0$

Parameter Estimation

Weighted least-square formulation (WLS)

Measured output errors

$$\min_{\theta} \quad \frac{1}{2}\sum_{k=1}^{NS}(y_k - y_k^*)^T V_y^{-1}(y_k - y_k^*)$$

$$s.t. \quad \frac{dx_k}{dt} = F(x_k, y_k, u_k, \theta, t)$$

$$0 = G(x_k, y_k, u_k, \theta, t)$$

$$x_k(0) = x_{k0}$$

$$\theta^L \le \theta \le \theta^U$$

- **End-point concentrations**
- **Reactor temperatures**

+ Smaller problem to solve.
- Ignoring input measurement errors.
- Fewer degree of freedom, less control.

Parameter Estimation

Errors-in-variables-measured formulation (EVM)

Measured output errors Measured input errors

$$\min_{\theta} \quad \frac{1}{2}\sum_{k=1}^{NS}(y_k - y_k^*)^T V_y^{-1}(y_k - y_k^*) + (u_k - u_k^*)^T V_u^{-1}(u_k - u_k^*)$$

$$s.t. \quad \frac{dx_k}{dt} = F(x_k, y_k, u_k, \theta, t)$$

$$0 = G(x_k, y_k, u_k, \theta, t)$$

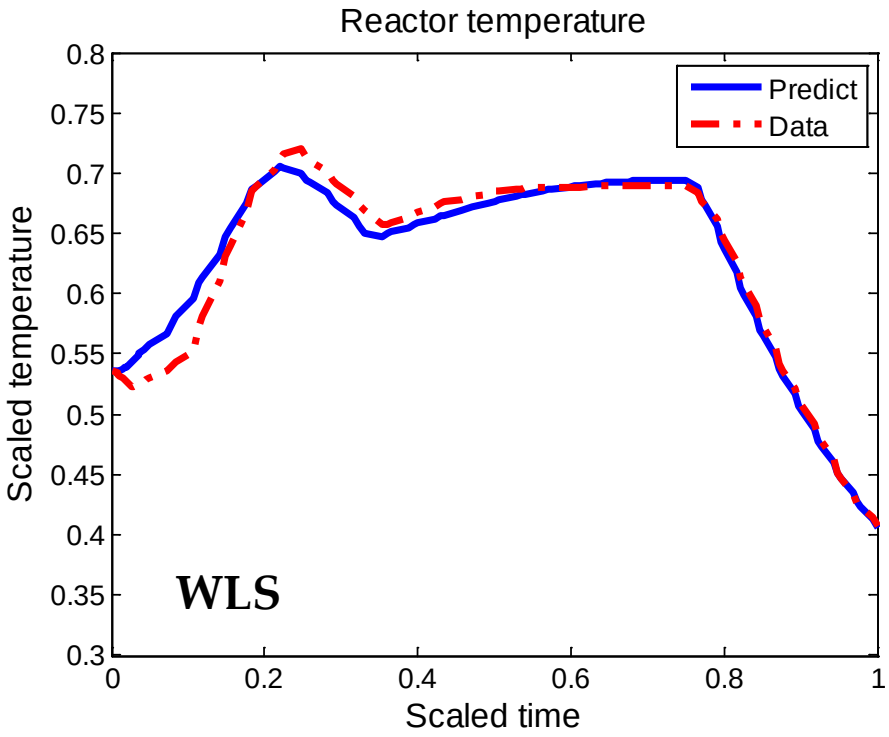
$$x_k(0) = x_{k0}$$

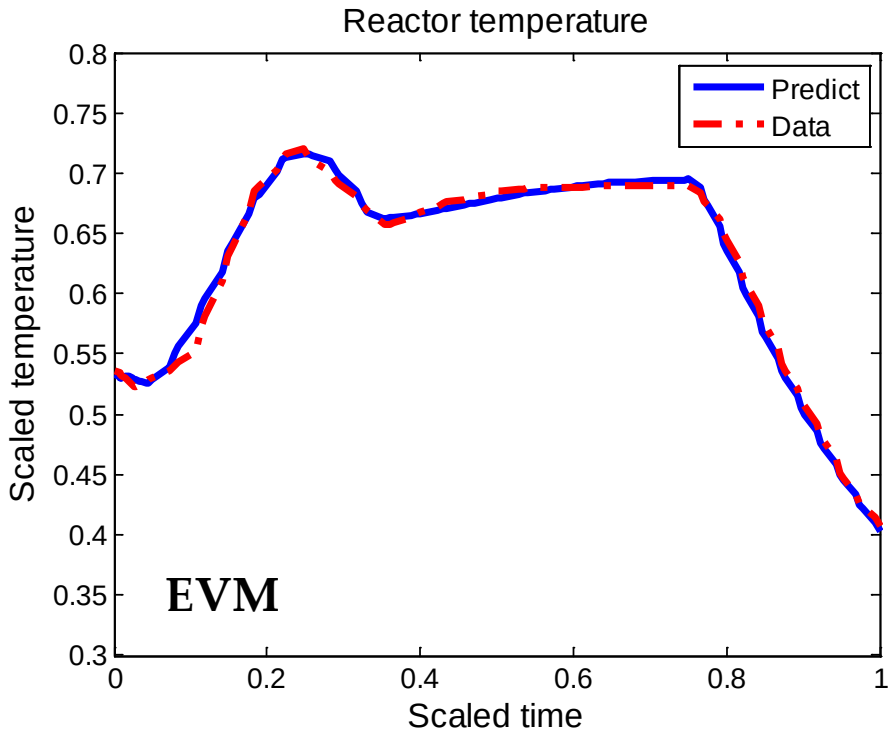
$$\theta^L \le \theta \le \theta^U$$

- End-point concentrations
- Reactor temperatures
- Jacket temperatures
- Weights and flowrates

+ Considering both input and output measurement errors.
+ Doing parameter estimation and data reconciliation at the same time.
+ More control of the problem, better data fitting.
- More decision variables, larger problem to solve.

Comparison of WLS & EVM





Fitting by EVM is much better than it by WLS.

Accumulated squared error of EVM is smaller than 1/3 of WLS.

Estimation Results

Estimated parameter values and confidence levels by EVM

Parameter	Estimated value (scaled P_i/P_i^0)	Variance $H^{-1}(i,i)$	Confidence level (σ_i/P_i)
A	0.507	0.0048	13.65%
B	0.97	0.0022	4.88%
D	0.446	2.6×10^3	11400%
E	0.805	0.005	8.78%
F	0.504	0.0094	19.26%
U_A	1	5×10^{-5}	0.71%
U_B	0.877	0.0011	3.8%
U_C	0.2	6.3×10^{-4}	12.56%

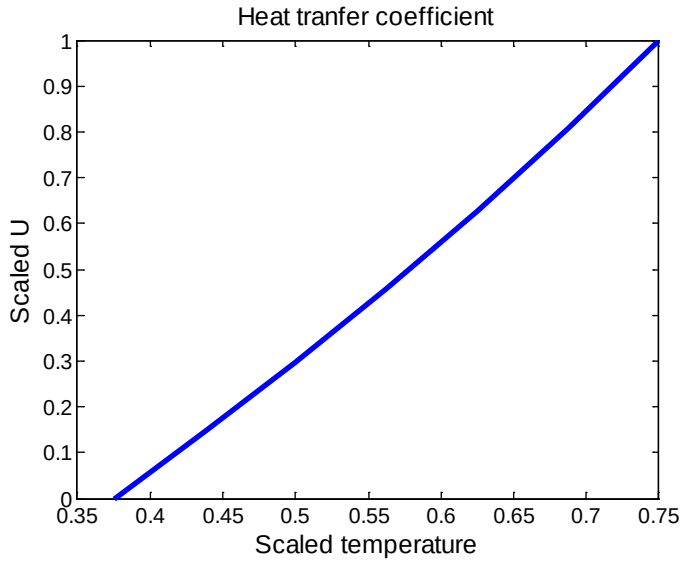
Large confidence level indicates the parameter is not estimable.

Parameter Selection

- Get rid of parameters with large confidence level → D

$$C_{b,X} = C_{s,X}$$

- Simplify heat transfer coefficient $U = \phi(T, \mathbf{U_A}, \mathbf{U_B}, \mathbf{U_C})$



$$U = \mathbf{U_A} + \mathbf{U_B} \times (T - T_0)$$

Estimation Results

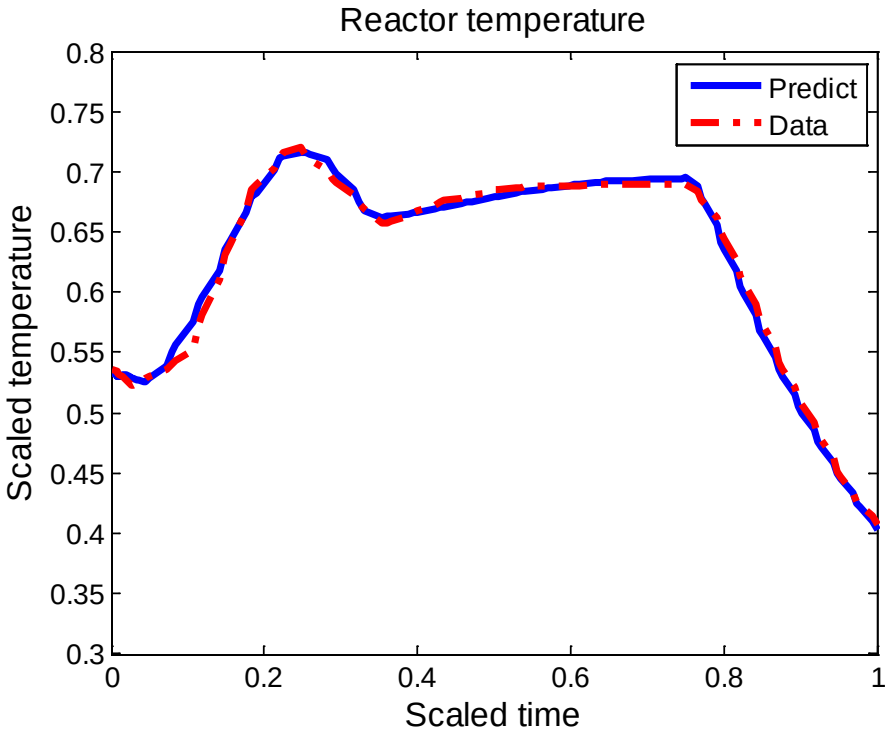
Modified estimation results

Parameter	Estimated value (scaled P_i/P_i^0)	Variance $H^{-1}(i,i)$	Confidence level (σ_i/P_i)
A	0.505	0.0046	13.42%
B	0.95	0.0021	4.83%
E	0.791	0.0047	8.69%
F	0.528	0.009	17.95%
U_A	0.305	2.8×10^{-6}	0.55%
U_B	0.374	5.62×10^{-4}	6.34%

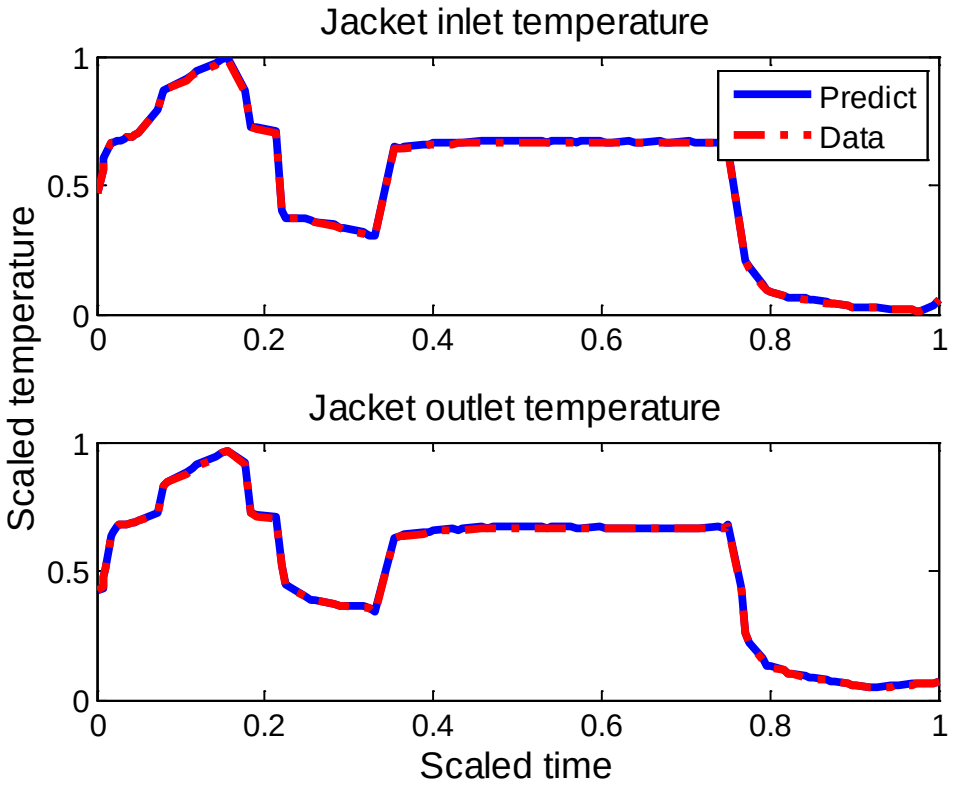
Small confidence level of all parameters.

Estimation Results

Data fitting



Fitting of reactor temperature (measured outputs)

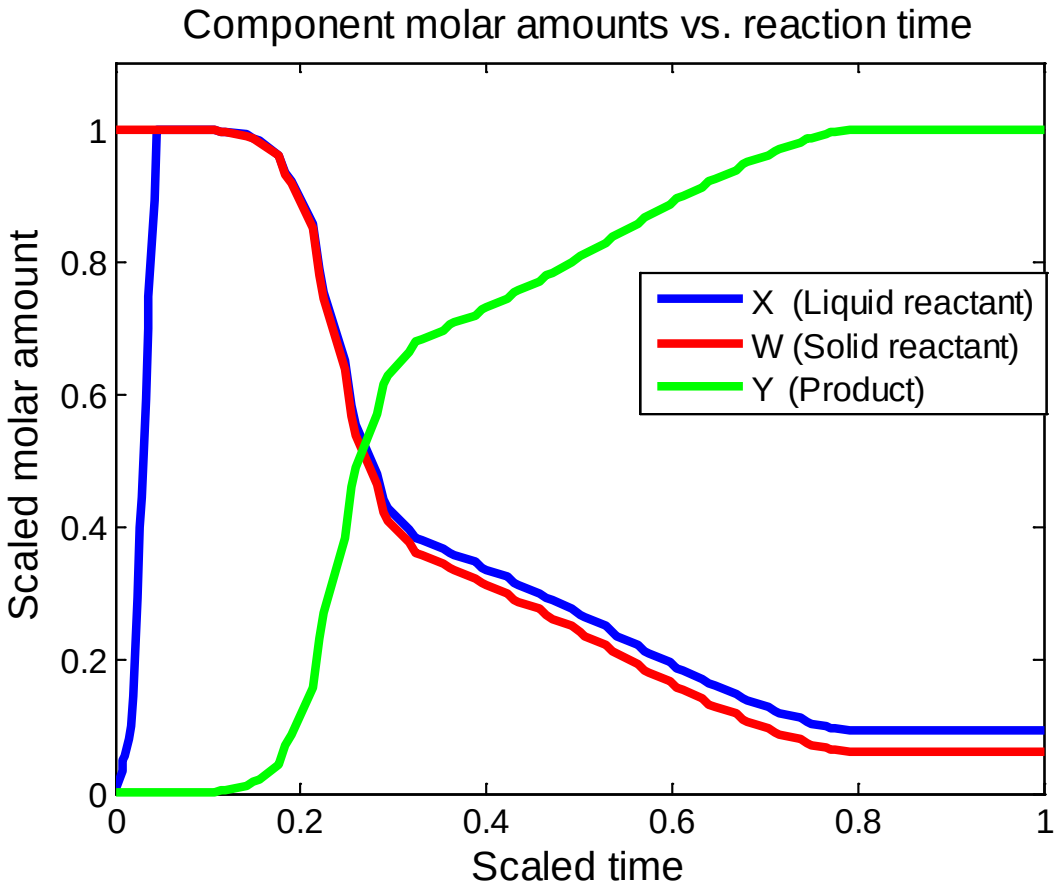


Fitting of jacket temperature (measured inputs)

Estimation Results

Reaction profiles

$$W(s) + X(l) \rightarrow Y(s/l) + Z(s)$$



Conclusion and Future work

- Shrinking particle and dissolution models of solid-liquid reactions are explored and an uniform dynamic model is implemented for both mechanisms.
- Parameter estimation is conducted based on limited industrial data. EVM method leads to better data fitting of both jacket temperatures and reactor temperatures.
- An analysis of estimation results is presented to enhance problem estimability.

- More data is going to be collected to validate the model.
- Recipe optimization and process control are going to be implemented after model validation.

References

- Forryan, Claire L., et al. "Heterogeneous kinetics of the dissolution of an inorganic salt, potassium carbonate, in an organic solvent, dimethylformamide." *The Journal of Physical Chemistry B* 109.16 (2005): 8263-8269.
- Salmi, Tapio, et al. "New modelling approach to liquid–solid reaction kinetics: From ideal particles to real particles." *Chemical Engineering Research and Design* 91.10 (2013): 1876-1889.
- Zavala, Victor M., and Lorenz T. Biegler. "Large-scale parameter estimation in low-density polyethylene tubular reactors." *Industrial & engineering chemistry research* 45.23 (2006): 7867-7881.
- Bard, Yonathan, and Yonathan Bard. *Nonlinear parameter estimation*. No. 04; QA276. 8, B3.. 1974.
- Biegler, Lorenz T. *Nonlinear programming: concepts, algorithms, and applications to chemical processes*. Vol. 10. SIAM, 2010.